PNC-CAT Microprobe Activities

Description of capabilities

Experimental highlights

- Sub-nsec time resolved XAFS
- GU program
- PNNL work
- Microbeams applied to Hanford cleanup

Basic beamline capabilities

- ID line
  - Si (111) (4-28 keV) and Si (311) (9-50 keV) rapidly exchangeable
  - Bendable toroidal focusing mirror can focus anywhere in B or C hutches
- BM line
  - Si (111) for 2.4 to 30 keV operation
  - Harmonic rejection/vertical focusing mirror
  - Sagittal bender being installed for horizontal focusing

Operational History

- ID line
  - First beam (FOE) late 1997
  - Limited experiments – mid 1998
  - Operational May 2000
  - 25% GU time Mid 2001 (35% in 2004)
- BM line
  - First beam March 2000
  - Unfocused operations Mid-2000
  - Informal scheduling of GU's starting in 2001
  - Scheduling 50% GU time now

Current On-site Staff

- Steve Heald – manager, microprobe experiments
- Dale Brewe – software development, time resolved experiments
- Julie Cross – diffraction and XAFS
- Robert Gordon – Canadian user support, UHV chambers
- Mali Balisubramanian – BM line support, XAFS
- Mike Pape – General user support, safety officer
- Tim Smith – Beamline controls specialist, computer support

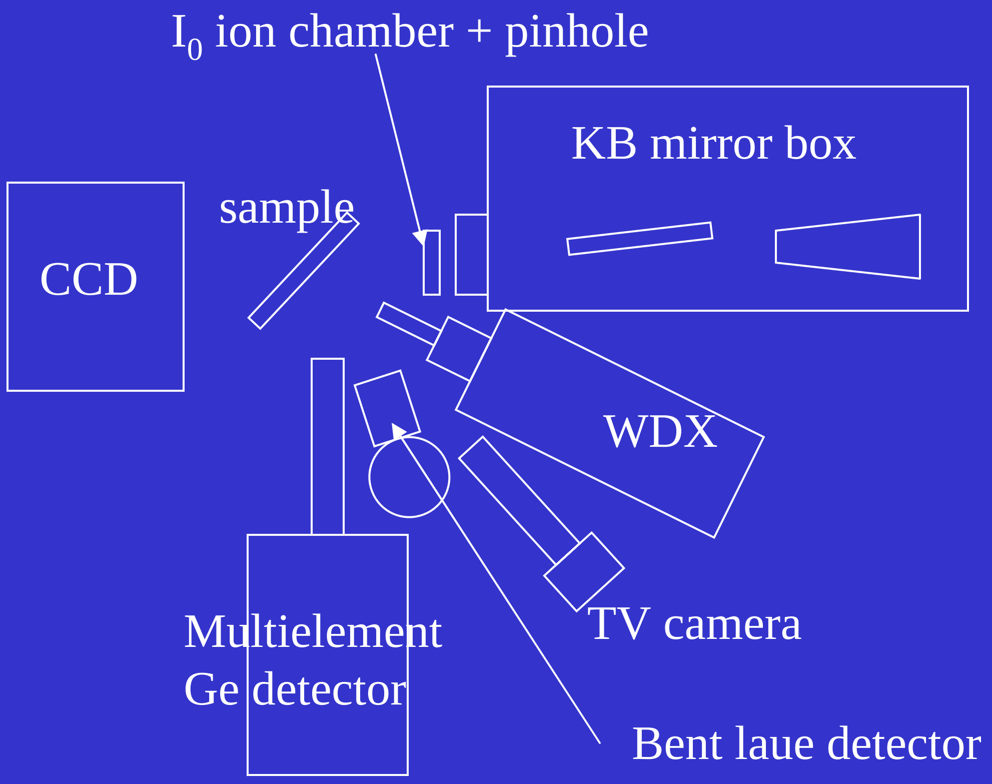
Microprobe facilities

- 3 KB mirror systems
- Dedicated microprobe station in 20-ID-B
  - 1-2 or 4-5 micron beam
  - Easy to change mirrors
  - Multiple detection options
- BM line microprobe just commissioned
  - 4-5 micron beam
  - Similar capabilities but 1000x less flux
  - Also used with laser experiment in 20-ID-C
- 50-60% ID beam time uses microprobe

Typical microprobe setup

Multiple simultaneous detectors possible

Low temperature (-30C) sample stage available



Microbeam Usage 20-ID

For the last and current cycle:

Total usage:

- 261/370 shifts used microbeams
- 23/29 experiments

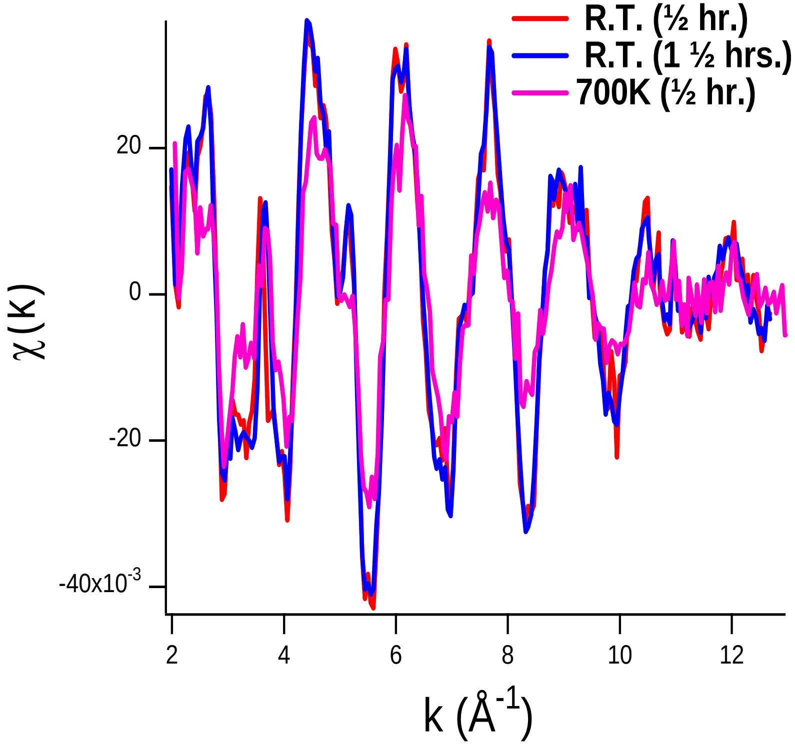
For general users:

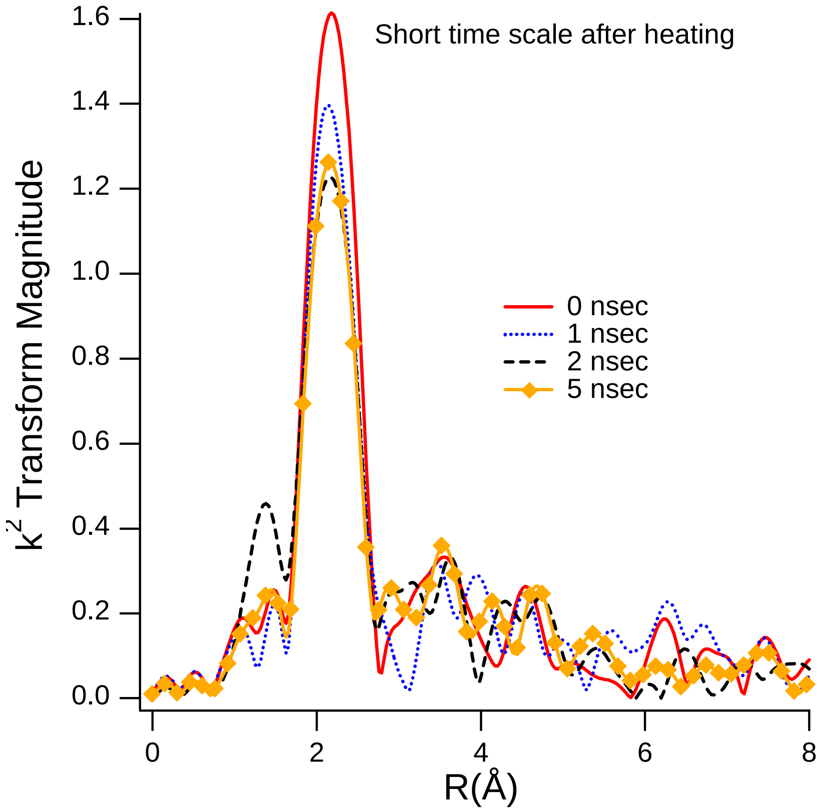
- 131/183 shifts
- 13/16 experiments

High Efficiency pump-probe experiments

- Femtosecond laser operating a 272 kHz – use all the x-ray photons from one bunch
- Approximately 4 μJ/pulse and a laser focus of 50 μm or less will melt/ablate most materials
- Use K-B mirrors to provide a 10 μm probe beam
- Fluorescence XAFS on thin film in <1 hr.
- Applied to heating dynamics in Ge

Preliminary Results for Laser-heated Germanium

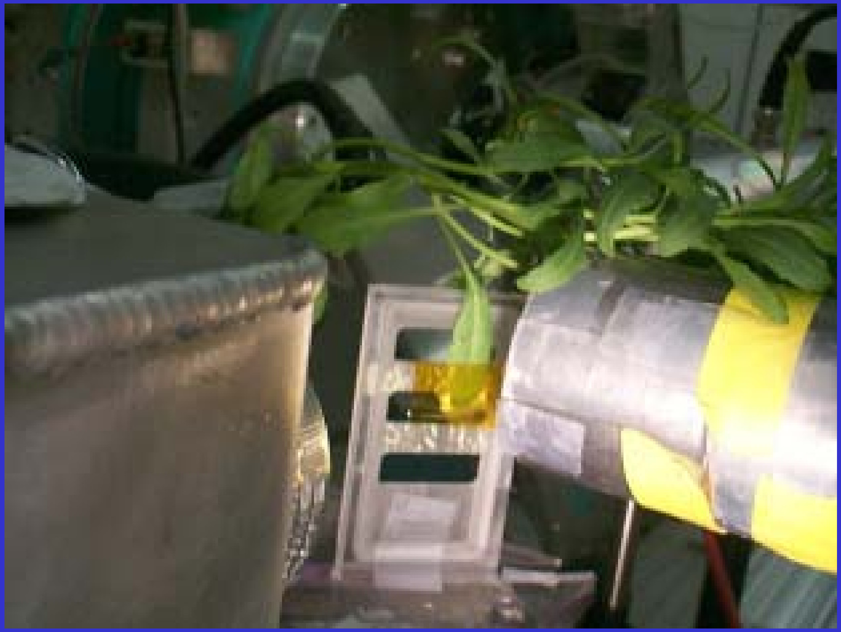




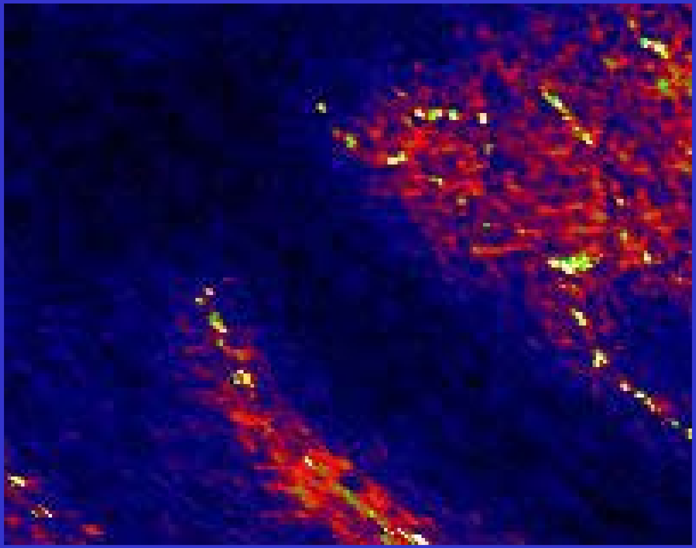
BM line microprobe

Useful for trial experiments, samples with higher concentrations, or samples subject to radiation damage

Hyperaccumulating plants – courtesy of Kirk Scheckel (EPA)



Thallium image

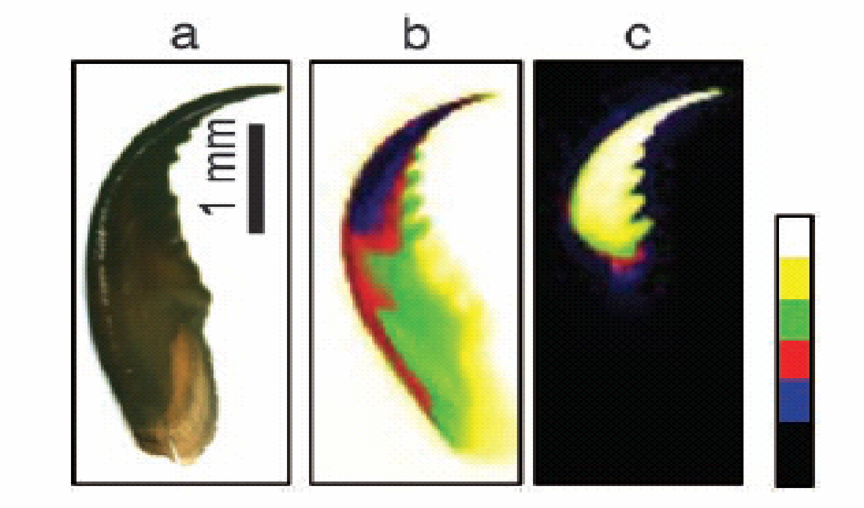


Some GU experiments on ID line

- As a popular element
  - MicroXAFS of As in U mine tailings (several Canadian groups)
    - See Paktunc etal, Environ. Sci. Technol. **37**, (10) 2067, (2003)
  - As in plants, plant roots, and single cell plants
- MicroXAFS of Sr in fossil corals
- Microbial degradation of radioactive waste containing cements
- Microspectroscopy of metals in breast tissues

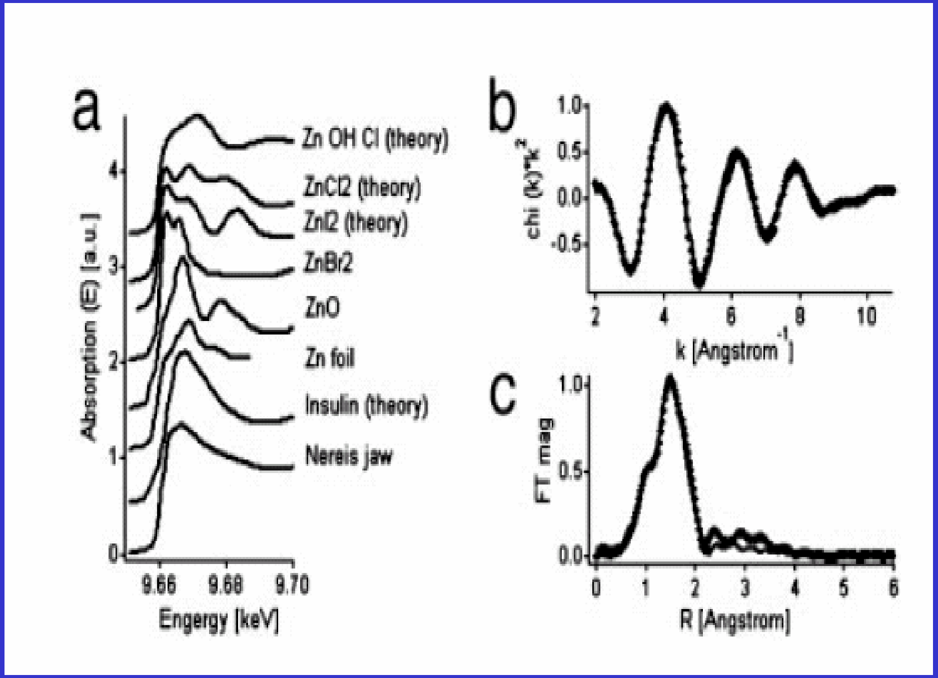
Zinc and mechanical prowess in the jaws of Nereis, a marine worm (Lichtenegger etal PNAS, 100, 9144 (2003))

Zn located in jaw tip where maximum strength needed



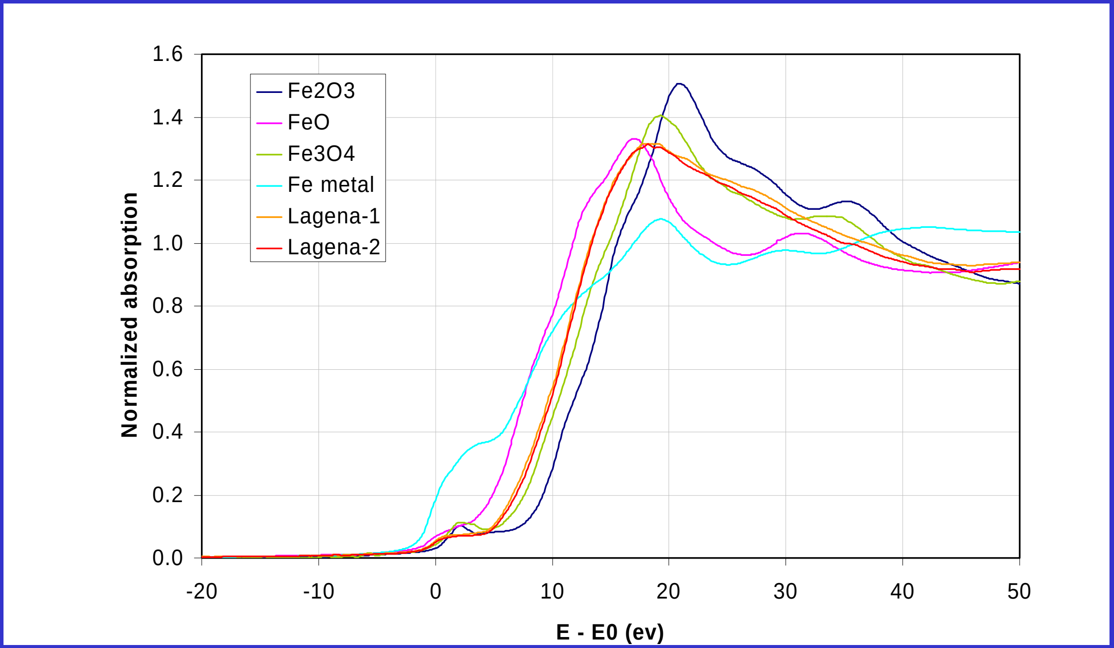
Optical Abs. Zn fluor

EXAFS indicates Zn in protein matrix



Magnetic sensors in pigeon brains (Lindseth etal)

- Fe nanoparticles in pigeon brain thought to be responsible for magnetic field sensitivity
  - Imaging to locate the particles
  - MicroXAFS to determine valence and structure:



PNNL projects using the PNC-CAT Microbeam

Imaging reduced zones on mineral surfaces (Amonette)

Reduction of uranyl by micas (Ilton)

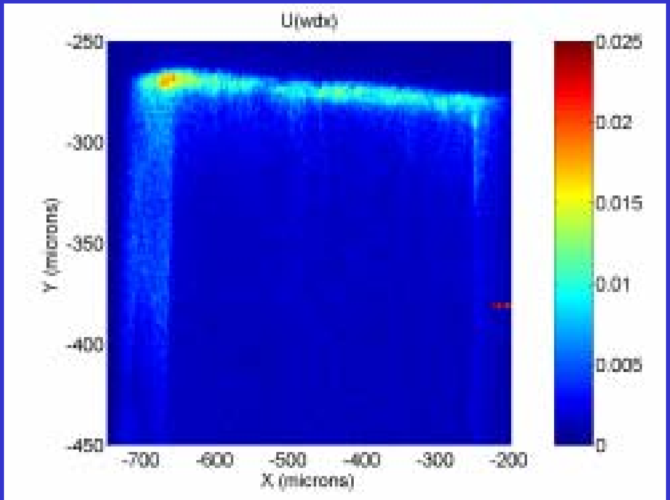
Characterization of U at Old Rifle remediation site (Long)

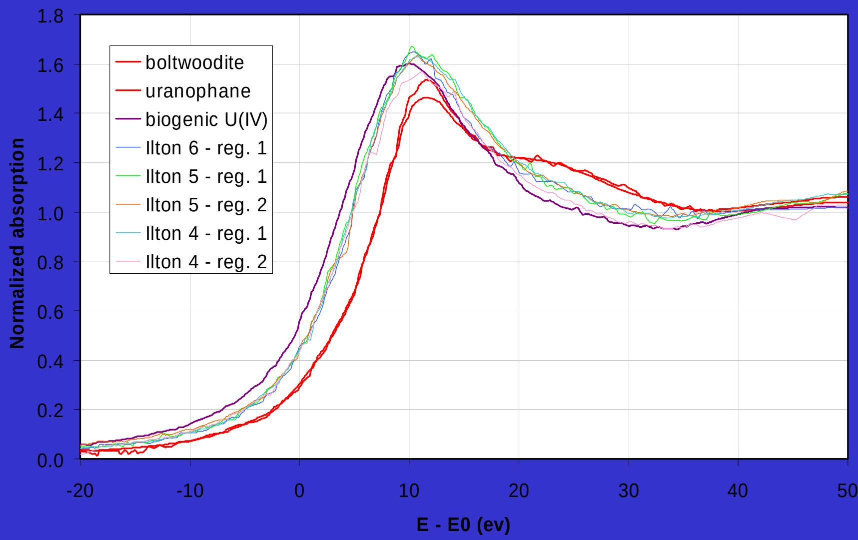
Role of anaerobic bacteria in Tc reduction (Zachara)

Fate of U in Hanford sediments (Zachara)

Heterogeneous Reduction of Uranyl by Micas

see Ilton etal, *Geochim. Cosmochim. Acta* in press





U enters edge of mica at ppm levels

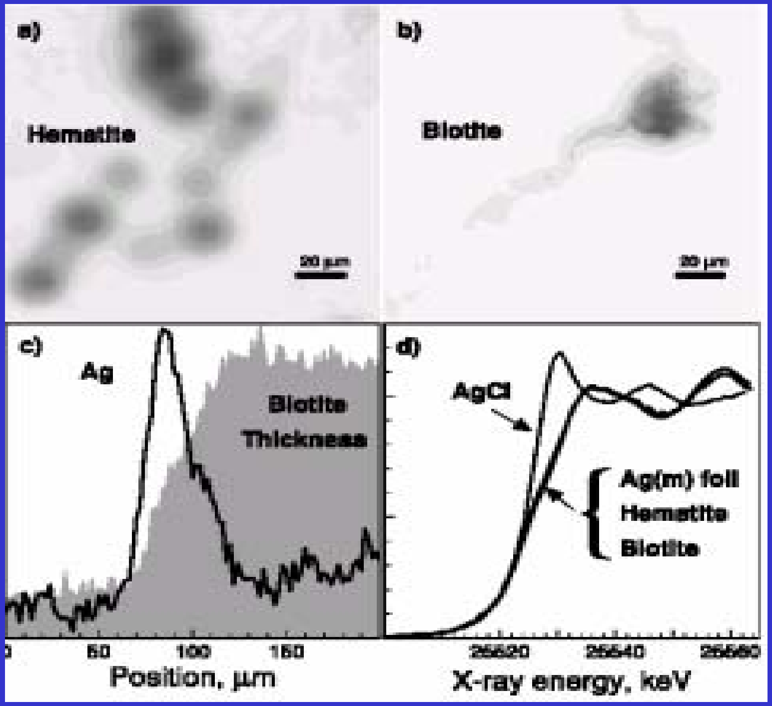
Near edge confirms reduction of uranyl

Proposal funded to extend work to phyllosilicates

New method for imaging reduced zones on mineral surfaces

see J. E. Amonette, S. M. Heald, and C. K. Russell, Phys. and Chem. of Minerals, 30,559 (2003).

Ag(I) preferentially deposits on Fe(II) regions
- Image the Ag to obtain a map of Fe(II) against large Fe(III) background



Line scan shows Ag deposited at edge where Fe(II) exposed

Near edge shows Ag(I) converted to metal

Work in support of Hanford cleanup

Extensive studies of fate of Cr, Cs, Tc and U in Hanford sediments

- Cs adsorption on micas
- Pertechnetate reduction in sediments
- Chromate reduction

Fate of released U from two sites:

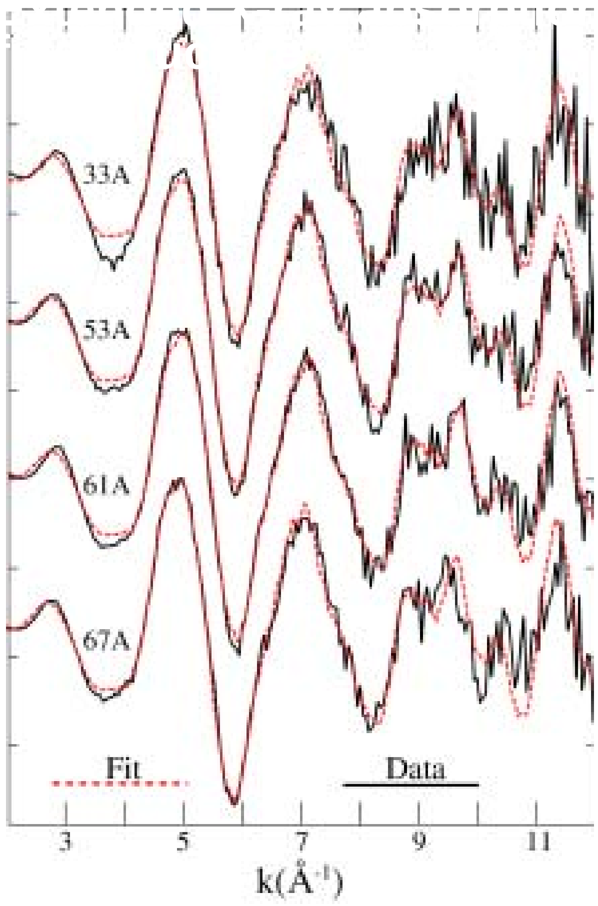
- B-BX-BY tank farm
  - transport of U less then expected
- 300 area contamination site
  - transport of U greater then expected

A Big Problem in Hanford's B-BX-BY Tank Farm: 10 Tons of Lost Uranium

- Hanford S&T program (EMSP & EM40)
  - Focused on major/intractable site problems
  - Managed by FSD/ETD
  - Involves 6 national laboratories
  - Over 10 universities

Bulk X-ray Absorption Spectroscopy of U(VI)-Containing Hanford Sediment

(Performed with Stanford Univ. Collaborators at SSRL)

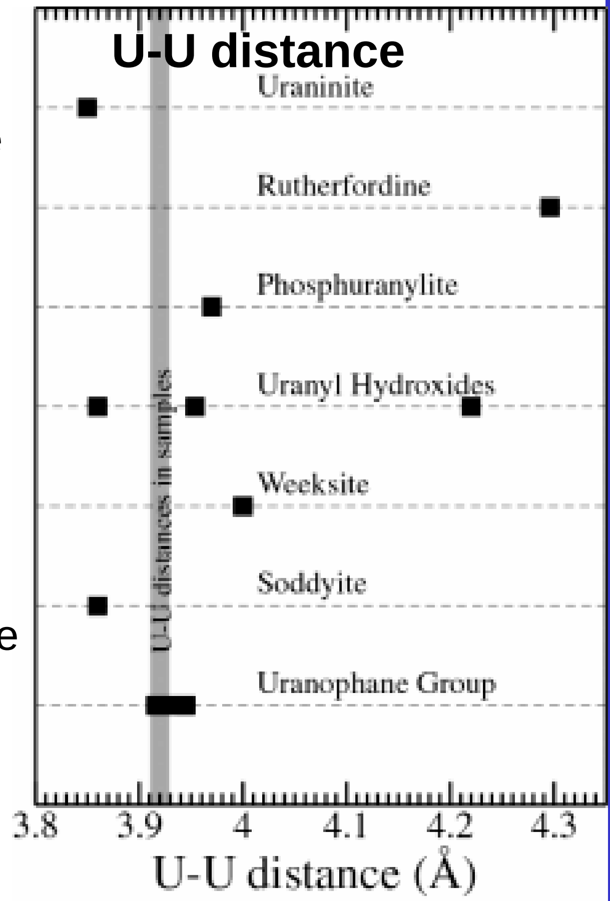


102% Uranophane
residual = 0.674

99% Uranophane
residual = 0.240

98% Uranophane
residual = 0.212

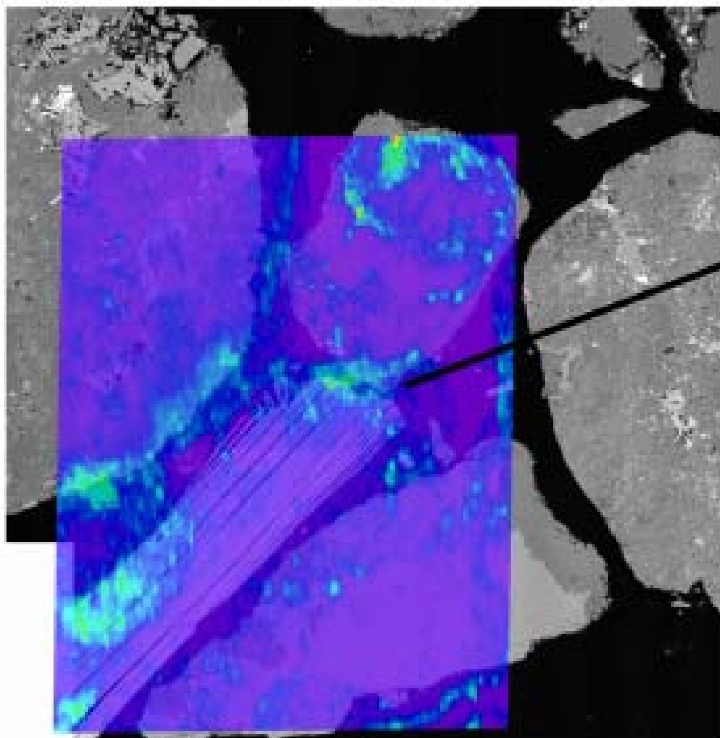
100% Uranophane
residual = 0.348

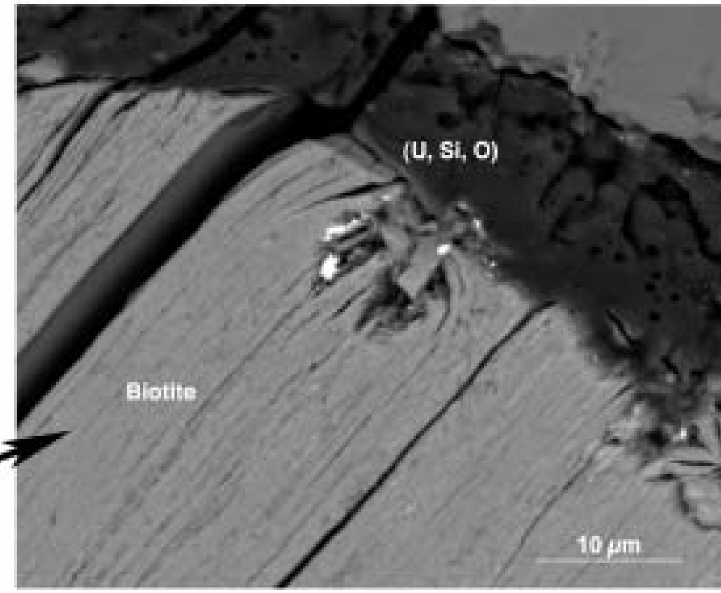


Uranophane = $Ca(H_3O)_2(UO_2)_2(SiO_4)_2(H_2O)_3$

XRM and SEM Analyses of U(VI) Containing Hanford Sediment

Uranium abundance (XMP)
Overlain on backscattered electron image

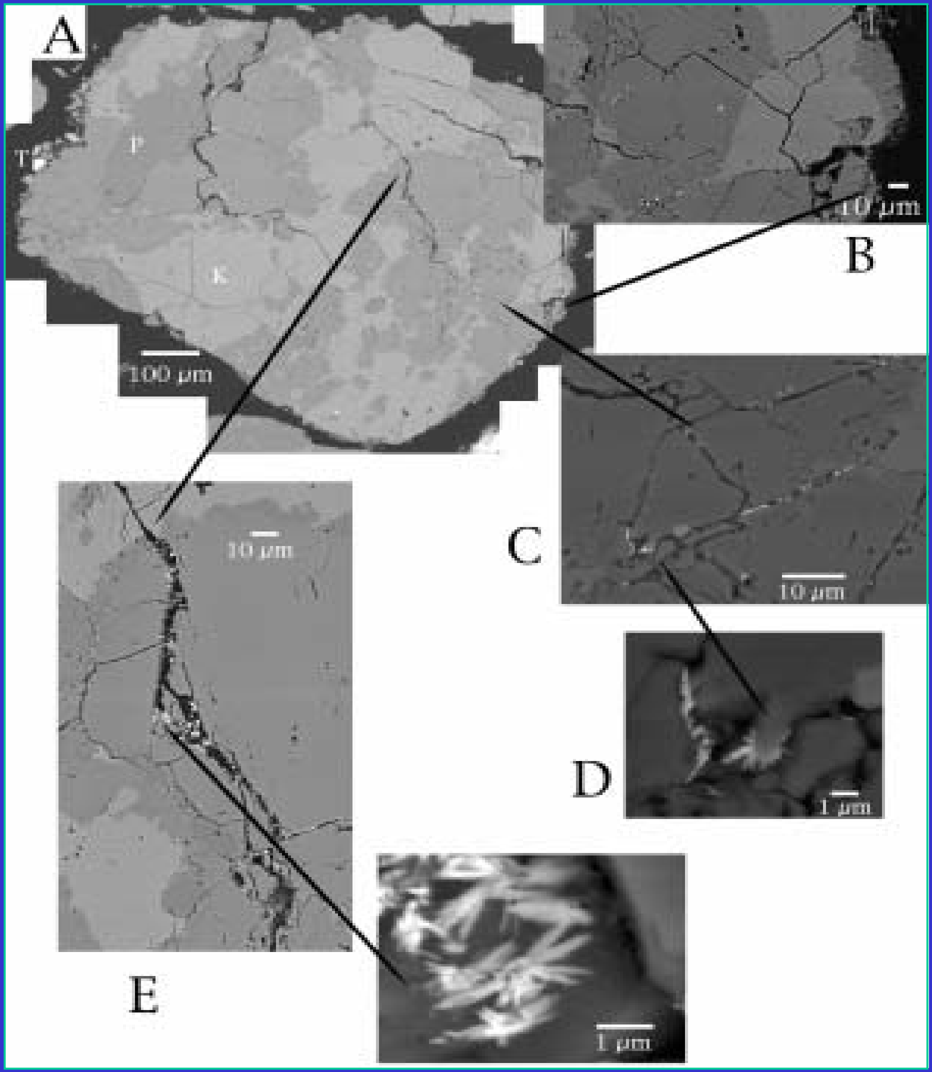




Detail backscattered electron image showing uranium silicate precipitates at biotite edge.

Composition information by EDS

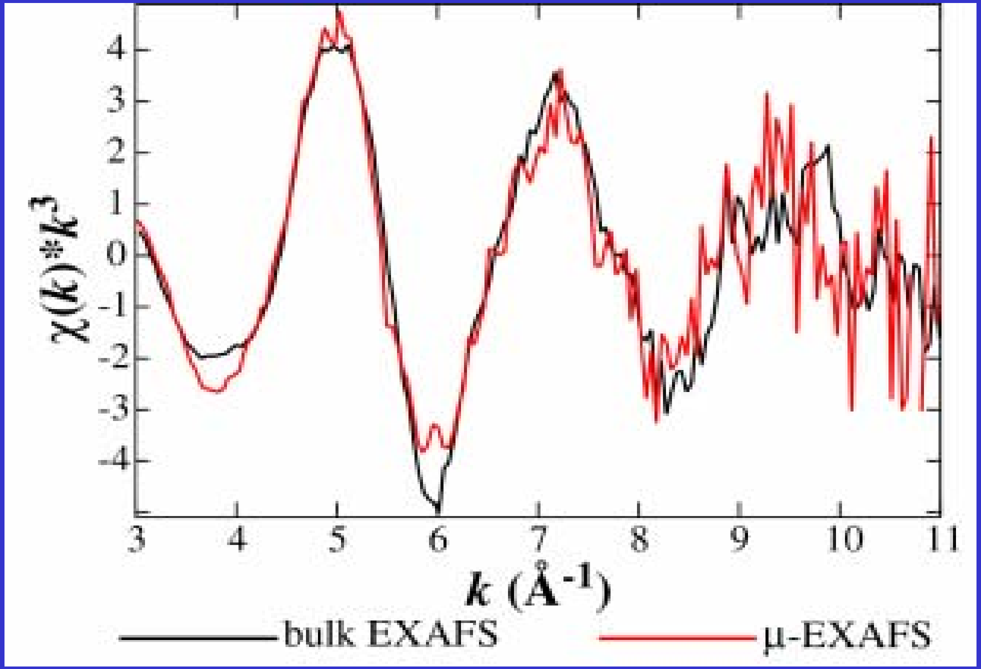
U(VI) Microprecipitates Exist within Grain Fractures of Quartz and Feldspar in BX-102 Sediment 61



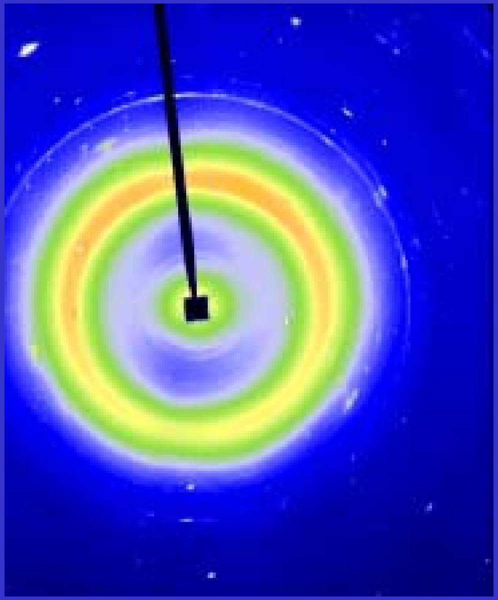
EXAFS and micro-EXAFS

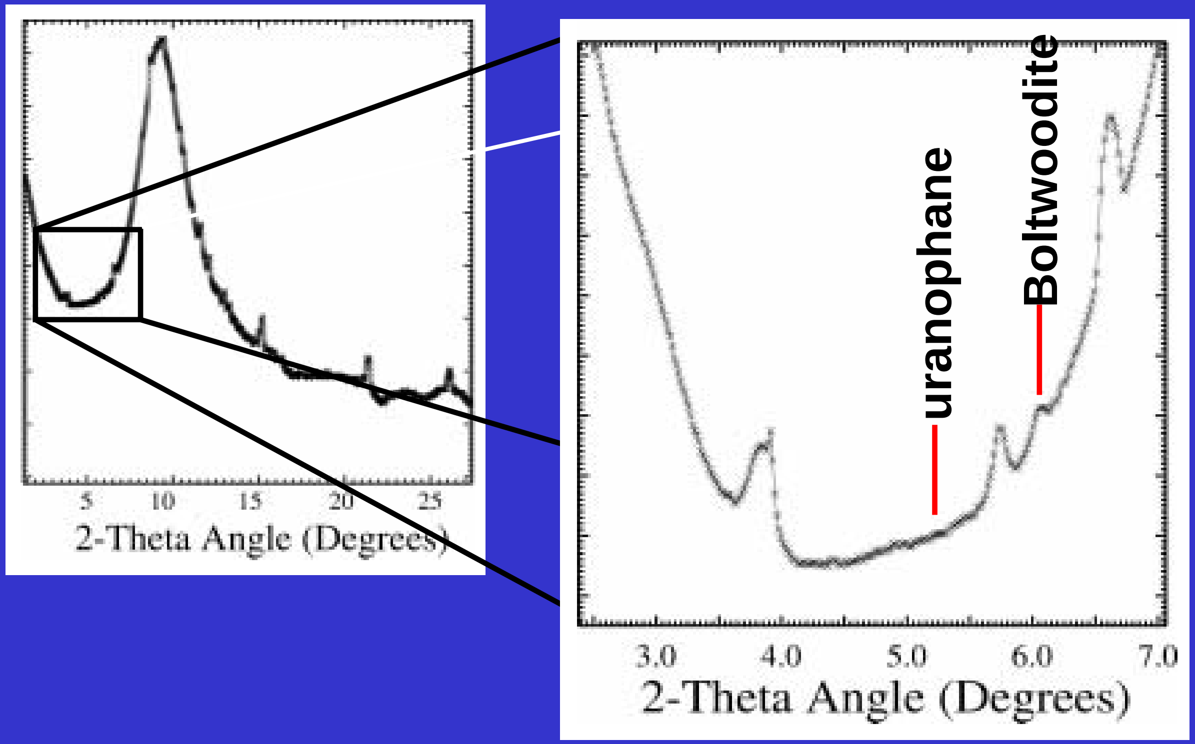
Bulk XAFS established U phase as likely Uranophane/Boltwoodite

Micro-XAFS confirms local region representative of bulk

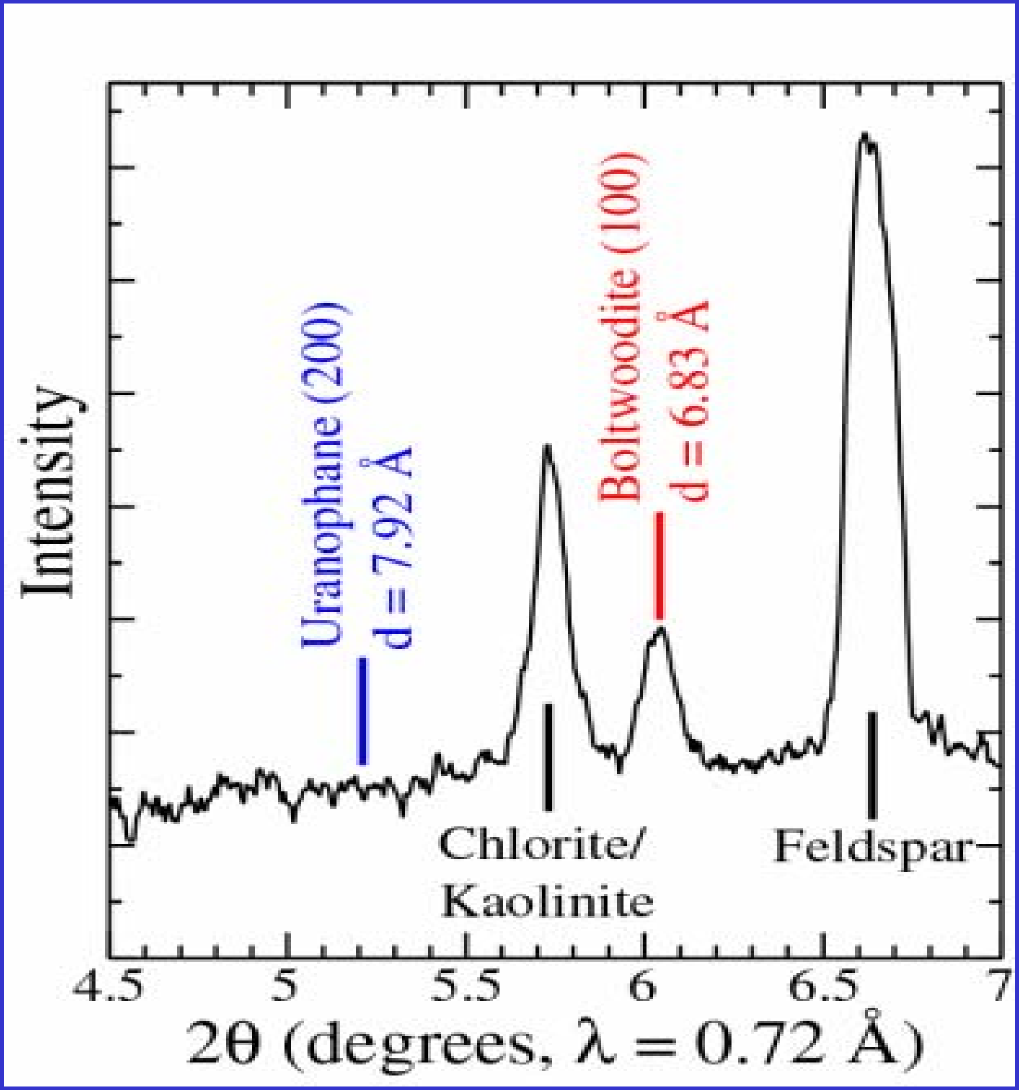


Micro-diffraction





Micro-diffraction (background removed)



Intraparticle Diffusion Model

Objective: Provide insights on key factors controlling intra-grain U(VI) precipitation

Boltwoodite precipitation

$UO_2(CO_3)_2^{2-} + Na^+ + H_4SiO_4 + 1.5H_2O = Na[UO_2(SiO_3OH)](H_2O)_{1.5} + 3H^+ + 2CO_3^{2-}$

Components

UO_2^{2+}, CO_3^{2-}, H_4SiO_4, Ca^{2+}, Na^+, NO_3^-, H^+, K^+, and Al^{3+}

Species

$UO_2CO_3^\circ$, $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, $UO_2Ca_2(CO_3)_3^\circ$, CO_3^{2-}, HCO_3^-, H_2CO_3, $H_4SiO_4^\circ$, $H_3SiO_4^-$, Ca^{2+}, Na^+, NO_3^-, H^+, K^+, $Al(OH)_4^-$, $Al(OH)_3^\circ$

Diffusivity

1×10^{-9} m^2/sec

Nucleation sites

4 precipitation sites between X/L = 0 to 1. Only the cells containing these site locations were allowed to precipitate

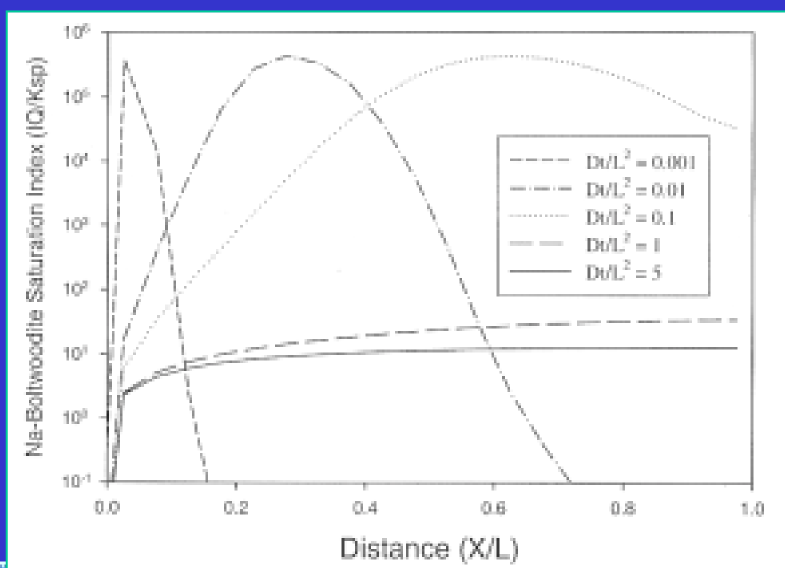
Micro-environment in cracks leads to Uranyl mineral growth

Modelling based on Na-Boltwoodite:

$UO_2(CO_3)_3^{2-} + Na^+ + H_4SiO_4 + 3OH^- = Na(UO_2)(SiO_3OH)\cdot(H_2O)_{1.5} + 1.5H_2O + 2\ CO_3^{=}$

Micro-environment much different from equilibrium

- Plagioclase feldspar serves as reservoir of silica
- Also buffers the high pH of waste fluid



Positive saturation remains at fracture interior even in steady state

Summary of B-BX-BY uranium work

XAFS and micro-diffraction important for determining uranyl phase and to constrain kinetic modeling

Boltwoodite is likely the dominant precipitated phase

Unique micro-environment leads to enhanced precipitation and entrainment of U in cracks

Dissolution studies indicate current conditions reasonably stable (should limit the infiltration of meteoric water)

300 area U plume

High visibility site that discharges into Columbia river

Currently no remediation as natural attenuation expected

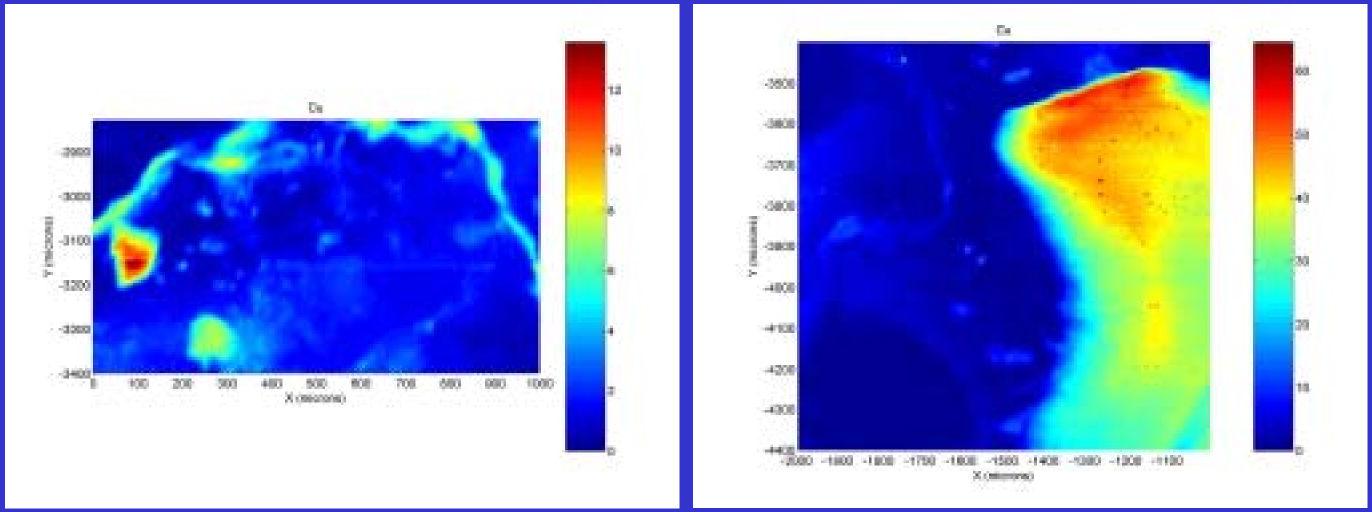
No decrease in groundwater U in spite of source removal

Rigorous conceptual model urgently needed to improve groundwater predictions and suggest remedial actions

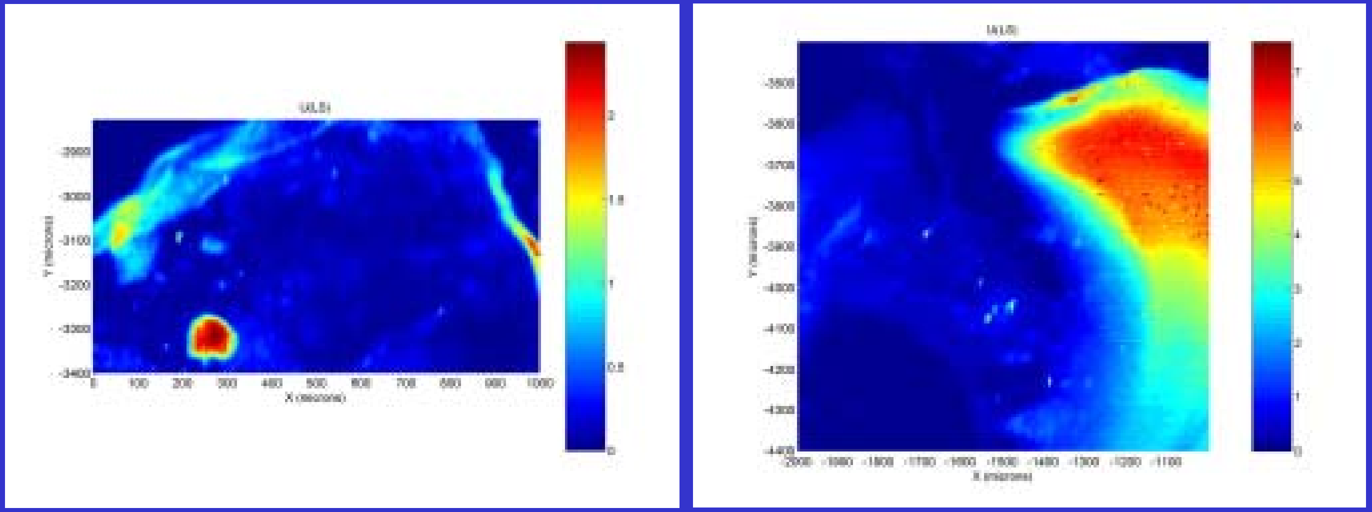
Unusual site with high concentration of Cu

Close association of U and Cu

Cu maps

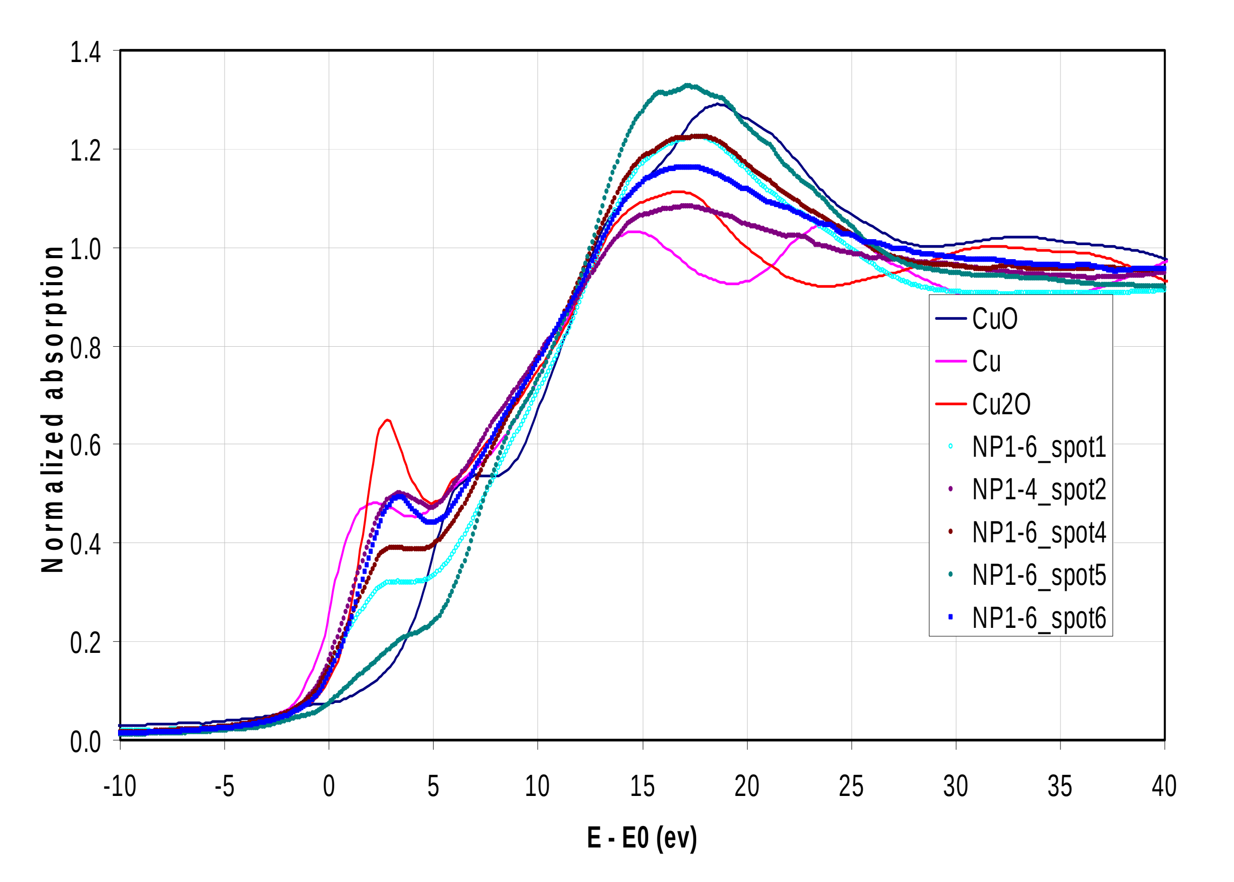


U maps

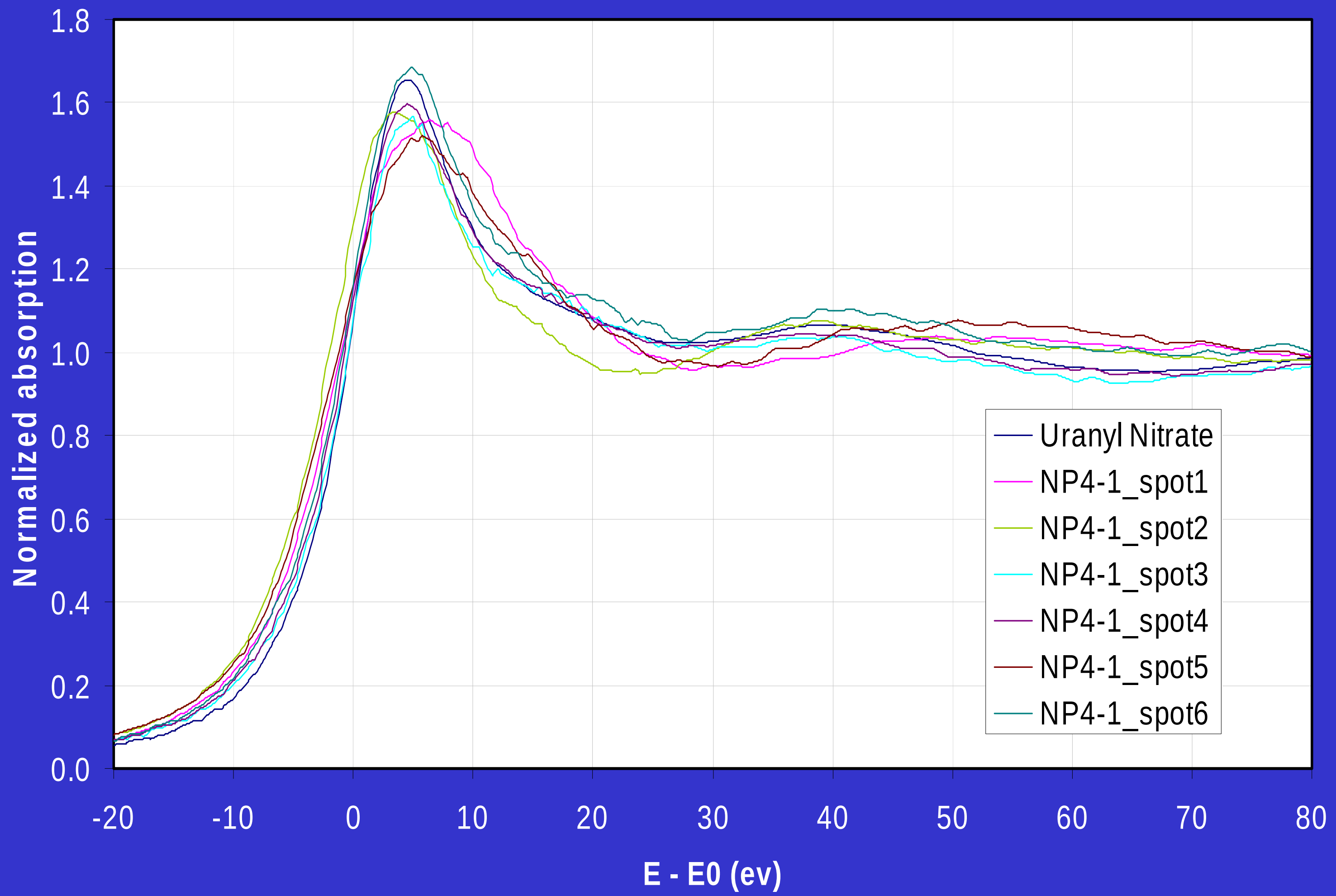


Cu(I) present in large quantities

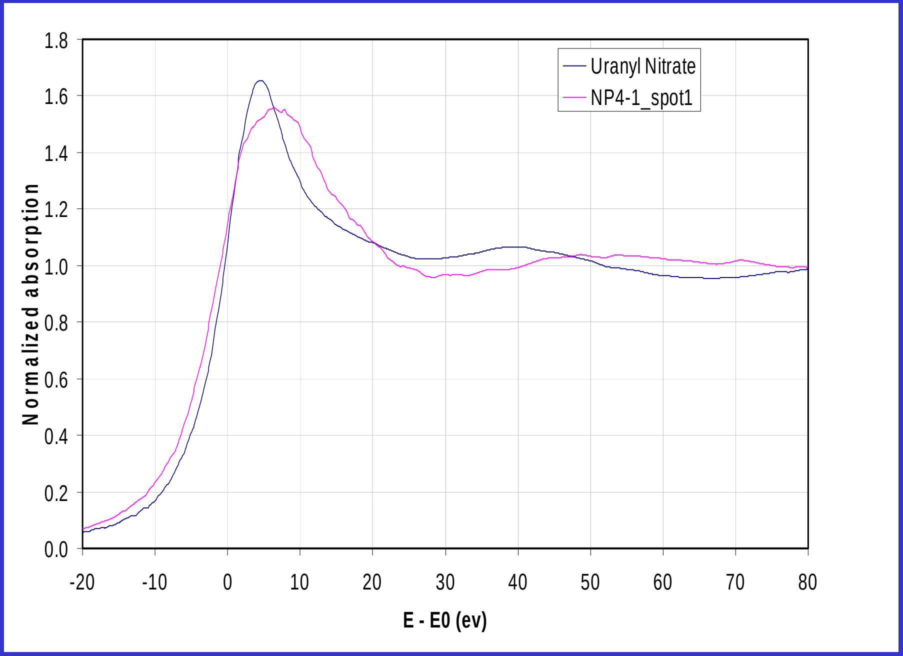
Cu(II) mostly in regions with lower U concentration

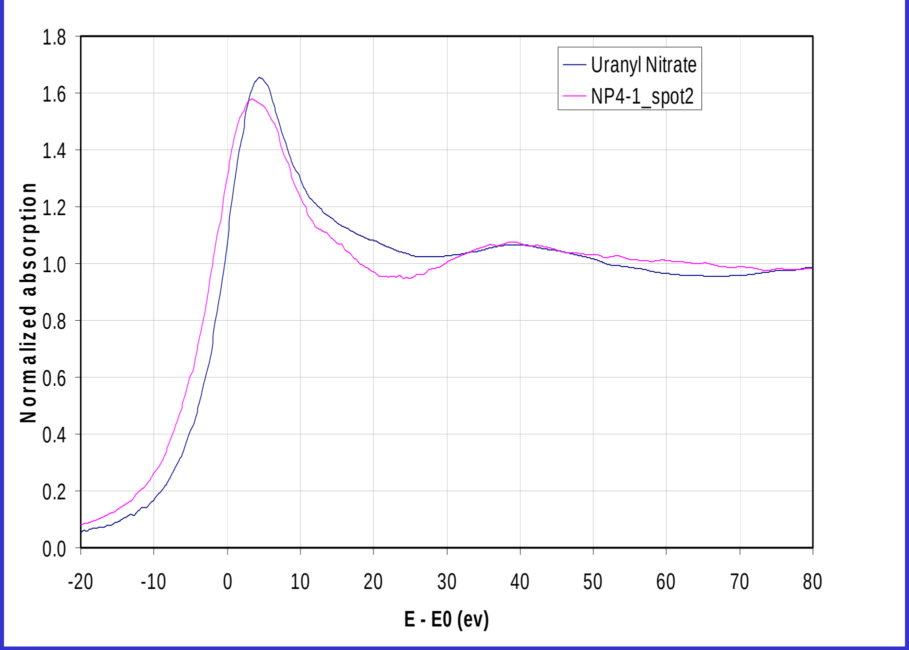


U valence varies

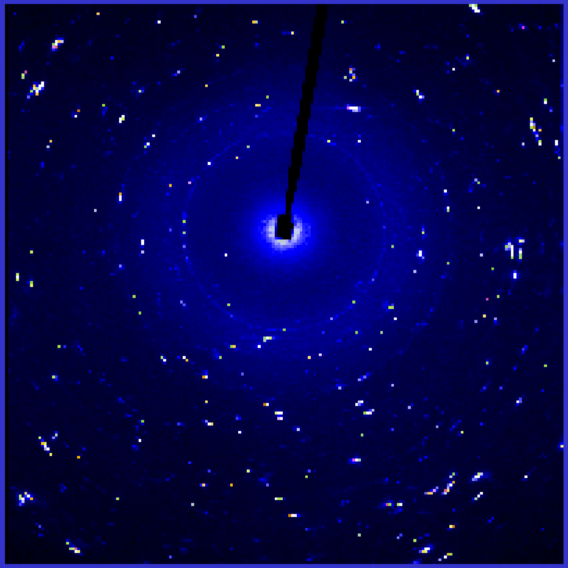


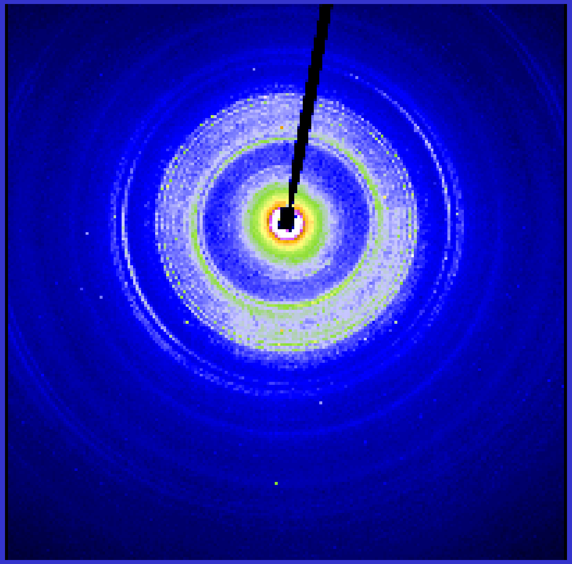
U phase likely varying also





Micro-diffraction obtained for all of the areas analyzed by XAFS





Collaborators on U work

PNNL - John Zachara, Jim Fredrickson, Jim McKinley, Chongxuan Liu, Odeta Qafoku, Zheming Wang

Stanford - Gordon Brown and Jeff Catalano

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